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PROVISIONAL SPECIFICATION FOR THE INVENTION ENTITLED:

"MANUFACTURE OF FLAT DISPLAY PANELS"

This invention is described in the following statement:-

FIELD OF THE INVENTION

This invention relates to methods of making display devices using light emitting diodes (LEDs) such as polymer or organic light emitting diodes as active layers. The method involves the direct deposition of LEDs or filters for LEDs such as patterned luminescent doped polymers and the fabrication of organic light emitting diodes (OLED's) and other semiconductor devices from these organic films.

RELATED ART

There is increased interest in light emitting diodes made from organic polymers because of their potential low cost and potential applicability to colour flat panel displays. The organic materials are typically deposited by spin-coating (in the case of polymer materials), or by evaporation (in the case of small organic molecules). In either case, the single material covers the substrate so that only devices of a single colour can generally be fabricated. The straightforward integration of multiple organic layers (for the fabrication of red, green, and blue emitters as pixels for colour displays) requires the patterning of the individual organic layers. Because of their solubility in and sensitivity to aqueous solutions and many solvents, such patterning of organic materials by conventional photoresist and wet processing techniques is difficult. Efforts to date to integrate organic light emitting diodes (OLED's) from materials which emit different colours on the same substrate such as through the use of cathodes evaporated through shadow mask as dry-etch masks have not been fully successful. Alternatively, the issue has been avoided all together by putting the three devices on top of each other.

Different colours can be obtained in light emitting diodes by placing red, green and blue filter materials onto white LEDs or by placing red, green and blue emitting materials in proximity to each other using photoresist patterning and etching techniques to transfer the photoresist pattern into the polymer; however, such photoresist techniques are inapplicable to organic materials because the chemicals uses for the photoresist process are incompatible with organic materials. Similarly, patterning subsequent layers on top of the organic (such as metal contacts) is difficult for the same reason. Vacuum deposited organic layers and metals may be

patterned by evaporating them through shadow masks, but this technology is difficult to extend to large areas and small pixel sizes and consequent registration problems.

One of the attractive feature of polymer or organic light emitting diodes is their very simple architecture. A basic device consists of an anode which is preferably indium tin oxide on a glass or plastic substrate, two thin polymer layers are then used, one of which is a polymer hole conducting layer (which can be a film of polyethylene dioxythiophene polystyrene sulphonate (PEDT/PSS) and the other of which is a conjugated polymer emissive layer. Then on the back a reflective cathode is provided. The whole device is then encapsulated to prevent the ingress of water. This invention in one form relates to the deposition in particular of one of more of the thin polymer layers.

There has been proposed the use of ink jet technology for the deposition of the polymer layers for OLEDs or the dyes for the polymers for OLEDs but there can be problems with this method of manufacture. This technology has problems with droplet size, processing time, registration and droplet bounce. The viscosity of the "ink" is also limiting for the deposition of polymers.

Light emitting diode arrays may be passive or active matrix arrays. Passive array are powered directly by conductor arrays and active matrix arrays include single or poly-transistor switching to provide more even activation of the LEDs. This system uses switching conductor arrays and separate power supply for the LEDs. The method according to this invention may be applicable to either type of LED array but is particularly applicable to active matrix arrays.

It is the object of this invention to provide an alternative method of manufacture of multi-colour light emitting diode or light emitting polymer arrays for flat panel displays.

BRIEF DESCRIPTION OF THE INVENTION

In one form therefore although this may not be the only or broadest form the invention is said to reside in a method of manufacturing a flat screen of display the type having separately illuminable pixels,

the method including the steps of;

i) providing a substrate having a light emitting diode array defining a plurality of pixel sites, each pixel site including an electrode;

ii) applying an electric charge to the electrodes of selected ones of the plurality of pixel sites,

iii) providing a bath of a liquid composition adapted to apply a colourant, the liquid composition including an insulative liquid and electrically charged colourant particles of a selected colour;

iv) placing the substrate into the bath;

v) attracting the colourant particles to the selected ones of the plurality of pixel sites;

vi) removing the substrate from the bath;

vii) removing excess liquid composition from the substrate;

viii) fixing the colourant particles to the substrate; and

ix) repeating steps ii) to viii) to apply further colourant of other selected colours to other selected ones of the plurality of pixel sites.

Preferably the colourants include the colours red, green and blue.

Preferably the charge is applied to the selected ones of the plurality of pixel sites by activating selected ones of the LED array.

In one form of the invention the light emitting diodes may be organic light emitting diodes.

Preferably the insulative liquid is selected from hydrocarbon fluids, silicone fluids and perfluorocarbons as discussed below.

Preferably the colourant particle are charged droplets in the discontinuous phase of an emulsion or the colourant particles can be toner particles. The toner particles may comprise an active resin and a pigment or dye to provide the colourant.

Hence the emulsion of one form of the invention comprises the insulative liquid as a continuous phase and a liquid discontinuous phase which is immiscible with the continuous phase, the liquid of the discontinuous phase comprising or including a pigment or dye to provide the colourant.

The substrate may be selected from glass, polyester foil, polycarbonate, Mylar™, stainless steel and the like.

The substrate can include a coating of indium tin oxide (ITO) and this ITO coating can be patterned into an array of electrodes.

In an alternative form the invention is said to reside in a method of manufacturing a flat screen of display the type having separately illuminable pixels,
the method including the steps of;
i) providing a substrate having a conductor array defining a plurality of pixel sites, each pixel site including an electrode;
ii) applying an electric charge to the electrodes of selected ones of the plurality of pixel sites,
iii) providing a bath of a liquid composition adapted to apply a selected polymer film to the selected pixel sites, the liquid composition comprising an emulsion including a continuous phase comprising being an insulative liquid and a discontinuous phase being electrically charged droplets of or including a polymer to deposit the polymer film;
iv) placing the substrate into the bath;
v) attracting the droplets to the selected ones of the plurality of pixel sites;
vi) removing the substrate from the bath;
vii) removing excess liquid composition from the substrate;
viii) fixing the polymer to the substrate; and

ix) repeating steps ii) to viii) to apply further selected polymer film to other selected ones of the plurality of pixel sites.

The polymer may be any material which exhibits electroluminescence such as poly(phenylene vinylene) (PPV), polyarlene, polyvinylcarbazole (PVK) and polyfluorene. These materials may also be known as light emitting polymers (LEPs).

The polymer film can include dopants to provide red, green and blue organic light emitting diodes.

Preferably the charge is applied to the selected ones of the plurality of pixel sites by activating selected ones of the conductor array.

Preferably the insulative liquid is selected from hydrocarbon fluids, silicone fluids and perfluorocarbons and the substrate is selected from glass, polyester foil and polycarbonate, Mylar or stainless steel. Where the substrate is not a conductor and the function of a conductor is needed for onr of the electrodes of a LED then the substrate can include a coating of indium tin oxide (ITO).

In a still further form the invention is said to reside in a method of manufacturing a flat screen of display the type having separately illuminable pixels,
the method including the steps of;
i) providing a substrate having a conductor array defining a plurality of pixel sites, each pixel site including an electrode;
ii) applying an electric charge to all of the electrodes of the plurality of pixel sites,
iii) providing a bath of a liquid composition adapted to apply a selected polymer film to the selected pixel sites, the liquid composition comprising an emulsion including a continuous phase comprising being an insulative liquid and a discontinuous phase being electrically charged droplets of or including a polymer to deposit the polymer film;
iv) placing the substrate into the bath;

v) attracting the charged droplets to the selected ones of the plurality of pixel sites;
vi) removing the substrate from the bath;
vii) removing excess liquid composition from the substrate;
viii) fixing the polymer to the substrate;
ix) applying an electric charge to selected ones of the electrodes of the plurality of pixel sites,
x) providing a bath of a liquid composition adapted to apply a dye to the selected ones of the pixel sites, the liquid composition comprising an emulsion including a continuous phase comprising being an insulative liquid and a discontinuous phase being electrically charged droplets of or including the dye to deposit onto the polymer film;
xi) placing the substrate into the bath;
xii) attracting the charged droplets to the selected ones of the plurality of pixel sites;
xiii) removing the substrate from the bath;
xiv) removing excess liquid composition from the substrate;
xv) fixing the polymer to the substrate; and
xvi) repeating steps ix) to xv) to apply further selected dye to other selected ones of the plurality of pixel sites.

The polymer is preferably polyvinylcarbazol (PVK) and the dye is selected from coumarin 7, coumarin 47 and nile red.

Preferably the charge is applied to the selected ones of the plurality of pixel sites by activating selected ones of the conductor array.

Preferably the insulative liquid is selected from hydrocarbon fluids, silicone fluids and perfluorocarbons as discused below.

Preferably the substrate is selected from glass, polyester foil, polycarbonate, Mylar and stainless steel and may be flexible or rigid.

The electrodes may be highly reflective such as being silver to reflect light produced in the light emitting polymer as much as possible forwards.

In one form of the invention the polymer film fixed to the substrate is a photo conductor and step ix) is achieved by selective illumination of pixel sites. For instance the polymer polyvinylcarbazole (PVK) can be a photoconductor and may be charged and selectively discharged to enable electrostatic attraction of the charged emulsion droplets as required.

In an alternative form the invention is said to reside in a method of manufacturing a flat screen of display the type having separately illuminable pixels,
the method including the steps of;
i) defining a plurality of pixel sites on a substrate by generating a electrostatic array pattern on the substrate;
ii) providing a bath of a liquid composition adapted to apply a selected polymer film to the defined pixel sites, the liquid composition comprising an emulsion including a continuous phase comprising being an insulative liquid and a discontinuous phase being droplets of or including a polymer to deposit the polymer film;
iii) placing the substrate into the bath;
iv) attracting the droplets to the defined the plurality of pixel sites;
v) removing the substrate from the bath;
vi) removing excess liquid composition from the substrate;
vii) fixing the polymer to the substrate; and
viii) repeating steps i) to vii) to apply further selected polymer film to other defined pixel sites.

The polymer film may be provided twice at each pixel site to generate a OLED. The first polymer may be one which provides a hole conducting layer (such as a film of polyethylene dioxythiophene polystyrene sulphonate (PEDT/PSS) and the other plymer can be one which provides a conjugated polymer emissive layer. This latter polymer may be selected from any material which exhibits electroluminescence

such as poly(phenylene vinylene) (PPV), polyarlene, polyvinylcarbazole (PVK), and polyfluorene. The order of deposition will be determined by whether the OLED is being deposited from the back to the front or from the front to the back. Preferably the hole conduction layer is in front of the emissive layer.

The emulsion used in any of these forms of the invention may include a continuous phase, a discontinuous phase which is immiscible in the continuous phase, and a surfactant, the surfactant having a first part which is compatible with the continuous phase and a second part which is compatible with the discontinuous phase, characterised by the continuous phase having a high volume resistivity, the discontinuous phase being electrically charged and the surfactant being selected to not significantly reduce the volume resistivity of the continuous phase.

As discussed above the continuous phase is comprised of a liquid which is electrically insulative and although the characteristics of a particular system would have to be determined empirically it is expected that such a liquid would preferably have a volume resistivity of approximately 1×10^6 ohm-cm or greater.

The continuous phase may be selected from hydrocarbons such as hexane, cyclohexane, iso-octane, heptane, aromatic hydrocarbons, decalin and isodecane and commercially available mixtures of hydrocarbons such as the Isopars™ an Norpars™ made by Exxon. The continuous phase may also be selected from fluoro-chemicals including fluoro-carbon compounds. These fluoro-chemicals generally comprise from 2 to 16 carbon atoms and include, but are not limited to, linear, cyclic or polycyclic perfluoroalkanes, bis(perfluoroalkyl)alkenes, perfluoroethers, perfluoroamines, perfluoroalkyl bromides and perfluoroalkyl chlorides. One form of fluorocarbons are the Fluorinerts™ from 3M. The continuous phase may also be selected from silicone fluids such as polyphenylmethyl siloxanes, dimethyl polysiloxanes, polydimethyl siloxanes, cyclic dimethyl siloxanes and the like.

The continuous phase may also be a gel or highly viscous liquid.

The discontinuous phase is preferably non-aqueous. Where the discontinuous phase is non-aqueous it should be immiscible or substantially insoluble in the continuous phase.

The discontinuous phase may be a reagent of the types discussed above or it may be a solvent which carries the active chemical reagent. Alternatively the active chemical reagent may be a solid or insoluble liquid dispersed in the discontinuous phase.

The emulsions according to the invention may also include charge control agents such as ionic or zwitterionic compounds selected from metallic soaps wherein the metals include: barium, calcium, magnesium, strontium, zinc, cadmium, aluminium, gallium, lead, chromium, manganese, iron, nickel, and cobalt and the acid portion is provided by a carboxylic acid of generally but not limited to at least 6 carbon atoms, e.g., caproic acid, octanoic (caprylic) acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, linolic acid, erucic acid, tallitic acid, resinic acid, naphthenic acid, succinic acid and the like. Examples of metallic soaps include: aluminium tristearate, aluminium distearate, barium, calcium, lead and zinc stearates; cobalt, manganese, lead and zinc linoleates; aluminium, calcium and cobalt octoates; calcium and cobalt oleates; zinc palmitate; calcium, cobalt, manganese, lead and zinc naphthenates; calcium, cobalt, manganese, lead and zinc resinates and the like. Other suitable charge directors may include nonpolar liquid soluble ionic or zwitterionic charge director compounds such as sodium dioctylsulfosuccinate, zirconium octanoate and metallic soaps such as copper oleate. The charge control agent may also be lecithin and alkyl succinimide. Where the continuous phase is a fluorochemical the charge control agent may include a fluorine analogue of the above compounds.

An emulsion according to this invention may have a continuous phase which is present in the range of about 40 to 99.99 per cent by volume, a discontinuous phase which is present in a range of from about 0.01 to 60 per cent by volume, optionally

a surfactant which is present in a range of about 0.01 to 35 per cent by weight and a charge control agent which is present in a range of 0.01 to 10 per cent by weight.

For some applications the emulsions may be manufactured immediately prior to use and in such situations the surfactant may not be necessary.

Throughout this specification the term emulsions is used to indicate emulsions, mini-emulsions and micro-emulsions. Hence the emulsions according to this invention may be true emulsions, that is, emulsions which are formed by the input of mechanical energy such as by shaking, stirring or the like. Emulsions may be manufactured using a device such as a Sonicator, Ultra-Turrax or a Microfluidiser. Alternatively the emulsions may be mini-emulsions which form with the application of more energy than for a standard emulsion. Alternatively the emulsions may be micro-emulsions which form substantially spontaneously provided the correct conditions of temperature and chemical composition are present. Emulsions may have a droplet size of from about 100 microns down to 0.2 microns, mini-emulsions may have a droplet size from 1000 nanometres down to about 50 nanometres and micro-emulsions may have droplet sizes of from about 200 nanometres down to 1 nanometre. It will be noted that there is no hard and fast rule on the size ranges for each. Size ranges will depend upon the composition of each of the phases and the surfactant used and the method of preparation.

For this invention the particles or droplets of emulsion may range in size from 100 microns downwards depending upon the type of emulsion and the applications to which the emulsion is to be applied. Preferably the emulsions may have a size range from 50 microns down to 20 nanometres.

In general therefore the invention relates to the manufacture of display screens by the selective deposition of materials to form organic or polymer light emitting materials where in the material is carried in the charged discontinuous phase of an emulsion and a deposition site is defined by the formation of an electrostatic or electric field at that site.

Normally the colours red, blue and green would be deposited in an array to give a display screen. The substrate upon which the display screen is formed may be rigid or flexible. Voltages to power the display screen are in the order of 2 to 10 volts and hence such displays can conveniently be battery powered.

This then generally describes the invention but to assist with understanding reference will now be made to the accompanying examples.

An experiment was carried out to determine whether a charged emulsion would deposit on an oppositely substrate charged with an electrostatic pattern formed thereon. For this purpose an emulsion was formed with an insulative continuous phase and a discontinuous phase which included a dye and polymer dissolved in the discontinuous phase so as to protect the dye from both water and air during and after deposition. A substrate comprising a zinc oxide photoconductor was charged in its entirety then covered with a mask before exposure to light so as to form a charge pattern that was a replica of the mask.

The emulsion comprised the following:

Continuous phase	FC40	0.99ml
Discontinuous phase	1% Butvar 72 (w/v), 0.1% (w/v) crystal violet in DMSO	0.005ml
	1% (w/v)Atlox 4912 in DMSO	0.005ml

Crystal violet was supplied by George T. Gurr, Searle Scientific Services, Bucks, UK
FC40 is a fluorocarbon solvent manufactured by 3M.
Butvar 72 is polyvinyl butyral manufactured by Solutia.
Atlox 4912 is a 12-hydroxystearic acid polyethylene glycol copolymer manufactured by the Uniqema business of ICI.
DMSO was supplied by Ajax FineChem, Australia

It was found that the discontinuous phase deposited only in the area of the charge pattern not exposed to light, giving a violet colouration.

In a further experiment comparable results were obtained when the emulsion composition comprised a continuous phase of FC40 and a discontinuous phase incorporating a polymer, AOT as surfactant and the pink fluorescent dye Rhodamine B.

The emulsion comprised the following:

Continuous phase	FC40	0.99ml
Discontinuous phase	1% Butvar 72 (w/v), 0.1% (w/v) Rhodamine B Both in DMSO	0.005ml
	10% (w/v)AOT in DMSO	0.005ml

Rhodamine B was supplied by Sigma Chemical Co.

It was found that the discontinuous phase deposited only in the area of the charge pattern not exposed to light, giving a fluorescent pink colouration.

Emulsions tested in the above experiments were prepared using ultrasonic generators. For the experiments only small volumes are required and also the cost of the perfluorocarbons used as the continuous phase in the nonaqueous emulsions are high, therefore equipment must be able to emulsify the smallest volumes that are practically possible. The rule of thumb for the production of mechanical emulsions is that the higher the power input per unit volume the smaller the emulsion size also the lower the surfactant requirement. This is achieved by the following equipment.

Luke Ultrasonics Cleaning system: Power 360 watts, used for emulsification & slide cleaning. Equipment manufactured in Australia.

Sonics and Materials Vibra-cell Model CV-17 Probe System: Power 600 watts, used for emulsification 1/4" probe, controlled power and timed output.

Throughout this specification various indications have been given as to the scope of this invention but the invention is not limited to any one of these but may reside in two or more of these combined together. The examples are given for illustration

only and not for limitation.

Throughout this specification and the claims that follow unless the context requires otherwise, the words 'comprise' and 'include' and variations such as 'comprising' and 'including' will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

Dated this 30th day of June, 2003.

Raustech Pty Ltd
By its Patent Attorneys
MADDERNS